Wei Hua's Four-Parameter Potential

Comments

and Computation of Molecular Constants

α_e and $\omega_e x_e$

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Abstract

The value of adjustable parameter C and the four-parameter potential $U(r) = D_e \left[\frac{1 - \exp[-b(r - r_e)]}{1 - C \exp[-b(r - r_e)]} \right]^2$ has been expressed in terms of molecular parameters and its significance has been brought out. The potential so constructed, with C derived from the molecular parameters, has been applied to ten electronic states in addition to the states studied by Wei Hua. Average mean deviation has been found to be 3.47 as compared to 6.93, 6.95 and 9.72 obtained from Levine2, Varshni and Morse potentials, respectively. Also Dunham's method has been used to express rotation-vibration interaction constant (α_e) and anharmonocity constant ($\omega_e x_e$) in terms of C and other molecular constants. These relations have been employed to determine these quantities for 37 electronic states. For α_e, the average mean deviation is 7.2% compared to 19.7% for Lippincott's potential which is known to be the best to predict the values. Average mean deviation for ($\omega_e x_e$) turns out to be 17.4%

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which is almost the same as found from Lippincott's potential function.

I. INTRODUCTION

A knowledge of exact potential function which governs the interaction between atoms as a function of internuclear distance, is of fundamental importance in a wide variety of fields ranging from gas kinetics to stellar structure. Besides, potential energy (PE) curves provide a good deal of information about the molecular structure. Accordingly, a number of methods have been developed to obtain these curves and the most satisfactory technique for this purpose is RKR method [1–3], which is based on the experimental spectroscopic data. This approach is, however, limited to the region for which the spectroscopic data exist. To overcome this limitation, one resorts to either Dunham method or to analytical functions. In the former, term values are expressed as:

$$T = \sum_{i,j} Y_{i,j}(v + \frac{1}{2})^i J^j (J+1)^j, \tag{1}$$

where v and J are the vibrational and rotational quantum numbers, respectively, and the co-efficients $Y_{i,j}$ are related to spectroscopic constants. The formulation of analytical functions is based on the assumption that bonding potential curves can be fitted to a certain form of algebraic expression. A comparative study of the empirical potential functions by Steele et al [4] and by Varshni [5] revealed that of all the three-parameter potential functions those suggested by Morse [7], Varshni [5] and Levine [8] have small average absolute deviation from the RKR curve with their respective values as 3.68%, 2.31% and 1.98%. The corresponding Schrodinger equation can, however, be exactly solved only for Morse function.

Some time back Wei Hua [9], introduced a four-parameter (FP) potential function which apart from the usual three parameters viz. ω_e, r_e, D_e, contains a fourth parameter, b, which in turn, depends on an adjustable constant C. The value of C was chosen to minimize the absolute deviation of the calculated values from the corresponding RKR - values. Wei Hua studied 15 electronic states and found that FP curves fit the RKR curves more closely

compared to Morse curves. Moreover, the corresponding Schrodinger equation can be solved exactly for zero and approximately for non-zero total angular momentum [9]. Almost all the researchers who have put forward an empirical potential function including the FP potential or have performed the comparative studies, have confined themselves to the study of simple molecules H_2, O_2, N_2, CO, NO, hydrogen and alkali halides or to alkali oxides. With a view to test the applicability of FP potential to a wider range of molecules, Morsagh [10] carried out their comparative study for diatomic molecules containing sulphur. It was found that for outer wall of the potential curve $(r > r_e)$ the average mean absolute deviations from RKR curve for Morse, Varshni, Levine and four-parameter potentials are 1.34%, 2.09%, 2.67% and 0.7%, respectively. Encouraged by the results in respect of FP potential, we have now dwelt upon the significance of adjustable constant C and have assessed how faithfully the potential function predicts the values of molecular parameters α_e and $\omega_e x_e$. This communication is an outcome of these efforts.

II. THE RKR-METHOD

This method [1–3] provides the classical turning points,

$$r_{max} = \left[\frac{f}{g} + f^2 \right]^{\frac{1}{2}} + f,$$

$$r_{min} = \left[\frac{f}{g} + f^2 \right]^{\frac{1}{2}} - f \qquad (2)$$

where f and g depend on the experimentally determined molecular constants $(\omega_e, \omega_e x_e, B_e, \alpha_e)$ and are defined as

$$f = \frac{\partial S}{\partial U},$$

$$g = -\frac{\partial S}{\partial k} \qquad (3)$$

with

$$S(U, k) = \frac{1}{\pi (2\mu)^{\frac{1}{2}}} \int_0^{I'} \{U - E(I, k)\}^{\frac{1}{2}} dI \qquad (4)$$

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Here U is the potential energy and E(I,k) is the sum of vibrational and rotational energies of the molecule,

$$I = h(v + \frac{1}{2}),$$
$$k = \frac{J(J+1)h^2}{8\pi^2\mu} \tag{5}$$

μ is the reduced mass of the molecule . However, for the present work RKR potentials have been taken from the literature and the references are given in tables 1 and 3.

Accuracy of a potential function can be judged in two ways: first by its comparison with the curve obtained from the experimental data and second, by using it to evaluate unused constants and comparing these with the respective experimental values. In the reported work the findings have been subjected to both the tests.

III. POTENTIAL FUNCTIONS FOR COMPARATIVE STUDY

In the present work we have considered only those potential functions for comparative study, which fit more closely to the RKR potential curve [4]. The expressions for these potential functions and parameters α_e and $\omega_e x_e$ are as following:

(i) Morse potential [4,7]

$$U_M(r) = D_e \left[1 - e^{-a(r-r_e)}\right]^2, \tag{6}$$

$$\alpha_e = \left(\frac{6B_e^2}{\omega_e}\right)\left(\Delta^{\frac{1}{2}} - 1\right),$$
$$\omega_e x_e = \left(\frac{\omega_e^2}{4D_e}\right); \tag{7}$$

(ii) Varshni potential [5,6]

$$U_V(r) = D_e \left[1 - \frac{r_e}{r}e^{-b_V(r^2 - r_e^2)}\right]^2, \tag{8}$$

$$\alpha_e = \left(\frac{6B_e^2}{\omega_e\Delta^{\frac{1}{2}}}\right)\left(\Delta - 2\Delta^{\frac{1}{2}} + 2\right),$$
$$\omega_e x_e = \frac{B_e}{8}\left(8\Delta - 12 + 36 - \frac{56}{\Delta^{\frac{1}{2}}} + \frac{48}{\Delta}\right); \tag{9}$$

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(iii) Levine potential [4,8]

$$U_L(r) = D_e \left[1 - \frac{r_e}{r} e^{-b_{\mathrm{L}}(r^p - r_e^p)} \right]^2, \tag{10}$$

$$\alpha_e = \left(\frac{6B_e^2}{\omega_e} \right) \left(\frac{3}{4} \Delta^{\frac{1}{2}} - \frac{1}{2} \right),$$

$$\omega_e x_e = \frac{B_e}{8} \left(8\Delta - 12(p-1)\Delta^{\frac{1}{2}} + 8p^2 + 4 - \left[\frac{(20p^2 - 12p)}{\Delta^{\frac{1}{2}}} \right] + \frac{12p^2}{\Delta} \right); \tag{11}$$

(iv) Four- parameter potential [9]

$$U(r) = D_e \left[\frac{1 - \exp\{-b(r - r_e)\}}{1 - C\exp\{-b(r - r_e)\}} \right]^2 \tag{12}$$

The expressions for α_e and $\omega_e x_e$ for this potential have been obtained in Section IV.

Here, D_e is the dissociation energy, r_e is the equilibrium bond length and 'a' is related to force constant through

$$k_e = 2D_e a^2 = U''(r_e) \quad \text{with}$$

$$k_e = \mu\omega^2; \tag{13}$$

$$\Delta^{\frac{1}{2}} = ar_e; \tag{14}$$

$$b_{\mathrm{v}} = \frac{\frac{1}{2}\left(\Delta^{\frac{1}{2}} - 1\right)}{r_e^2}; \tag{15}$$

$$b_{\mathrm{L}} = \frac{p^{-1}\left(\Delta^{\frac{1}{2}} - 1\right)}{r_e^p}; \tag{16}$$

$$p = 2 + \frac{\frac{1}{4}(\Delta^{\frac{1}{2}} - 4)(\Delta^{\frac{1}{2}} - 2)}{(\Delta^{\frac{1}{2}} - 1)} \tag{17}$$

In order to obtain an analytical expression for C, we have compared FP potential with five-parameter potential function of Hulburt and Hirschfelder [11] because a potential function with large number of parameters is more flexible. This gives C as

$$C_{rel} = \left(-\frac{1}{12} + x \right) - \sqrt{ \frac{120}{144} - \frac{37}{48}x^2 - \frac{2}{12}x + \frac{17}{144}\frac{G}{ar_e^2} } \tag{18}$$

where

$$x = \frac{1+F}{ar_e},$$
$$F = \frac{\alpha_e \omega_e}{6B_e^2},$$
$$G = \frac{8\omega_e x_e}{B_e}$$

and

$$a = \sqrt{\frac{k_{\mathrm{E}}}{2D_e}} \qquad (19)$$

C has been denoted as C_{rel} to distinguish it from the C, obtained by minimum deviation method adopted by Wei Hua.

The values of C_{rel} have been computed for the electronic states studied by Wei Hua using the data listed in Table 1 and are compared with C (columns 3 and 4 in Table 2). Value of C_{rel} depends on B_e, α_e and $\omega_e x_e$, apart from other parameters viz. ω_e, r_e and D_e, that are used in almost all the three-parameter potential functions. In other words, the value of C_{rel} also depends on the rotational constants. Furthermore, it is observed that a small change in α_e changes C_{rel} significantly while a similar change in other parameters produces small variation. For example, in case of Li_2, if we change the value of either α_e or $\omega_e x_e$, then resulting variation in the value of C_{rel} due to the latter is nearly one-third that due to the former. Thus, C_{rel} is more sensitive to the rotation-vibration interaction constant compared to other parameters involved in the relation. Using the equation (18), values of C_{rel} for the electronic states studied by Wei Hua, have been calculated and this, in turn, has been used to calculate the FP potential curve.

Mean square deviations in

$$\Delta Y_j = \frac{\sqrt{\overline{\left(U_j - U_{RKR}\right)^2}}}{D_e} \qquad (20)$$

where j denotes four-parameter (FP), Morse (M), Levine (L), Varshni (V) potential functions, have been calculated for all the cases. The results are projected in Table 2. It has been found that the mean square deviations with C_{rel} are not far off from the corresponding values derived with C which makes us to have faith in their correctness. In view of this,

C_{rel} has been employed to calculate the potential curve for additional ten electronic states (Table 3) and deduce the values of α_e and $\omega_e x_e$ for a total of 37 electronic states of various molecules including the ones studied by Wei Hua.

IV. DERIVATION OF α_E AND $\omega_E X_E$

On the basis of wave mechanics Dunham [12] has shown that molecular parameters can be expressed in terms of the derivatives of potential functions if it can be expanded in the form of a power series. Applying this method, we get

$$\alpha_e = [ar_e(1 + C) - 1]\frac{6B_e^2}{\omega_e} \tag{21}$$

and

$$\omega_e x_e = \frac{h}{8\pi^2 c\mu}a^2(1 + C + C^2)$$
$$= B_e\Delta(1 + C + C^2) \tag{22}$$

where $B_e = \frac{h}{8\pi^2 cI}$ as obtained from the solution of equation for a rotator. The relation for α_e is of the same form as obtained by Pekeris [12] using the Morse potential function, viz.

$$\alpha_e = \left[\left(\frac{\omega_e x_e}{B_e}\right)^{\frac{1}{2}} - 1\right]\frac{6B_e^2}{\omega_e} = [ar_e - 1]\frac{6B_e^2}{\omega_e} \tag{23}$$

and that of Lippincott's relation [4] i.e.

$$\alpha_e = \left(\frac{6B_e^2}{\omega_e}\right)ab\Delta^{\frac{1}{2}} \tag{24}$$

where

$$a = \frac{4}{5}\left(1 - \frac{1}{b\Delta^{\frac{1}{2}}}\right);$$

and

$$b = 1.065 \tag{25}$$

The expression for $\omega_e x_e$ is to be compared with

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$$\omega_e x_e = \frac{B_e}{8}\left(3 + 12ab\Delta^{\frac{1}{2}} + 6\Delta + 15a^2b^2\Delta - 12ab^2\Delta\right) \tag{26}$$

obtained from Lippincott's potential function [4].

Values of these two parameters have been calculated for 37 electronic states and are given in Tables 4 and 5 for α_e and $\omega_e x_e$, respectively. These Tables also include the corresponding experimental values and the values found by employing Morse (eqn. 7), Varshni (eqn. 9) and Lippincott's (eqns. 23, 26) potential functions. Values of molecular constants used in these calculations are listed in Table 1.

V. RESULTS AND DISCUSSION

The adjusTable constant C is determined by finding the mean square deviation of the FP potential from the RKR potential curve, which itself is calculated using the molecular parameters $\omega_e, \omega_e x_e, \alpha_e, r_e$ and B_e of the individual energy levels [1–3]. Thus, any variation in the parameters from level to level is taken care of and hence most of the variations are absorbed indirectly. On the other hand, the least square fitted values of the parameters are used in the expression for C_{rel}. These values of parameters, therefore, do not take care of level to level variations. Inspite of this C_{rel} is quite close to the value of C calculated by minimum deviation method. Among the electronic states which were studied by Wei Hua [9] the values of C_{rel} are within $\pm6\%$ of the values of the C except for $\text{Li}_2\text{X}^1\Sigma_g^{+3}, \text{H}_2\text{X}^1\Sigma_g^+, \text{COX}^1\Sigma_g^+$ and $\text{XeOd}^1\Sigma^+$ where the deviations are, respectively, 11%, 15.9%, 24% and 24%. These deviations can be understood from the fact that the molecular constants vary in going to higher energy levels. In Li_2, $v = 0$ to 4 and $v > 10$ levels have α_e values 0.00704 and 0.0077, respectively (corresponding γ_e values are also different). In the case of those electronic states for which complete and accurate data are available, C_{rel} is very close to C; the differences may be attributed to the fact that in C_{rel}, finer interactions are not included.

The mean square deviations of the FP potential with C (i.e. ΔY_{FPC}) and C_{rel}(i.e.$\Delta Y_{FPC_{rel}}$) from RKR potential curve have been compared in Table 2. The mean

square deviations are within $\pm 5\%$ except for those states for which C_{rel} departs significantly from C.

A stringent condition for the acceptance of a potential function is the exact solution of the corresponding Schrodinger wave equation. As discussed by Wei Hua [9], FP potential provides eigenvalues:

$$E_n = \frac{D_e}{4}\left[2 + (Q^2 + 1) - \frac{(\rho_c - \bar{n})^2}{t^2} - \frac{(Q^2 - 1)^2 t^2}{(\rho_c - \bar{n})^2}\right] \tag{27}$$

where

$$Q = \frac{1}{C}, t = \frac{2D_e}{\omega_e(1 - C)}, \bar{n} = n + \frac{1}{2}, n = 0, 1, 2, 3;$$

$$\rho_c = \text{sign of}(C)\rho \quad \text{and} \quad \rho = \left[\frac{1}{4} + (Q^2 - 1)^2 t^2\right]^2 \tag{28}$$

The mean square deviation of the energy values (E_{cal}) with $C(\Delta E_C)$ and $C_{rel}(\Delta E_{C_{rel}})$ from the observed levels (E_{obs} i.e. U_{RKR} values) have been calculated using the above equation and are given in the last two columns of Table 2. Corresponding ΔE_C and $\Delta E_{C_{rel}}$ are very close to each other supporting that C_{rel} equals C within the accuracy of molecular parameters and can be computed from these (eqn. 18). To reinforce the above conclusions, the mean square deviations viz. ΔY_j and $\Delta E_{C_{rel}}$ from the RKR potential have been compared for additional ten states using C_{rel} in the FP potential function and the results are compiled in Table 3.

Taking C_{rel} as the correct value of C parameters, α_e and $\omega_e x_e$ have been calculated using equation 21 and equation 22, for 37 electronic states including those studied by Wei Hua. The FP potential with C_{rel} yields α_e values within $\pm 15\%$ of the corresponding experimental values. The observed variation is a consequence of uncertainty in the values of the molecular parameters which, in turn, determine the accuracy of C_{rel}. It may, however, be pointed out that the results are closer to the experimental values as compared to the ones obtained from Lippincott's potential function (eqn. 24) which is claimed to be the best potential for predicting the α_e values [4]. The average mean deviations for FP, Morse, Varshni and

Lippincott's potentials are 7.2%, 27.6%, 18.7% and 19.7%, respectively, establishing the supremacy of FP potential over other three-parameter potentials in predicting the α_e values.

As regards $\omega_e x_e$ the average mean deviations have been found to be 17.4%, 26.9%, 15.5% and 13.9%, respectively for FP, Morse, Varshni and Lippincott's potential functions. Obviously, the accuracy is not as good as for α_e. This is perhaps because C_{rel} itself is not as much sensitive to $\omega_e x_e$. However, the results are better than the Morse potential for which, unlike the Varshni and Lippincott's potential functions, Schrodinger equation is solvable. The calculated values are slightly larger than the experimental values for almost all the molecules. A graph between C_{rel} for the individual level and r_{max} (corresponding to v) (fig. 1) reveals that C increases almost exponentially to large negative values at higher v. The nature of the curve at large v and the fact that the factor $(1+C+C^2)$ may be approximated to $e^C (= 1+C+\frac{C^2}{2})$ because $|C| < 1$, have prompted us to write $\omega_e x_e$ in the light of equation 22, as

$$\omega_e x_e = \frac{h}{8\pi^2 c\mu} a^2 e^C \tag{29}$$

The use of this relation reduces the average mean deviation to 15.9% (column 12 in Table 5) which is comparable to the value obtained from Lippincott's potential function.

VI. CONCLUSIONS

The constant C has been expressed in terms of molecular constants implying that the FP potential manifests the contribution of vibration, rotation, rotation-vibration interaction constants. Furthermore, the potential may be preferred over all the known three-parameter potentials for the prediction of the rotation-vibration interaction constant, α_e and it yields the value of $\omega_e x_e$ as good as provided by Lippincott's function which is known to be the best analytical function for its prediction.

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TABLES

TABLE I. Experimental Molecular Constants Used in this work.

S.No.	Molecular State	r_e (A^o)	D_e (cm^{-1})	ω_e (cm^{-1})	α_e $10^3(cm^{-1})$	B_e (cm^{-1})	$\omega_e x_e$	μ_e	Ref.

1.	$Li_2X^1\Sigma_g^+$	2.6729	8516.780	351.430	7.040	0.6726	2.6100	3.5080	17,14
2.	$Na_2X^1\Sigma_g^+$	3.0788	6022.600	159.177	0.873	0.1547	0.7254	11.4949	18,14
3.	$K_2X^1\Sigma_g^+$	3.9244	4440.000	92.405	0.212	0.0562	0.3276	19.4800	19
4.	$Cl_2X^1\Sigma_g^+$	1.9872	20276.440	559.751	1.516	0.2442	2.6943	17.4844	20
5.	$Cl_2B^3\Pi$	2.4311	3341.170	255.3800	2.511	0.1631	4.8000	17.48442	21
6.	$I_2XO_g^+$	2.6664	12547.335	214.520	0.113	0.0373_7	0.6079	63.4522	22,23
7.	$IClX^1\Sigma^+$	2.3209	17557.600	384.275	0.532	0.1142	1.4920	27.4147	24
8.	$IClA^3\Pi_1$	2.6850	3814.700	211.030	0.744	0.0852_9	2.1200	27.4147	24,25
9.	$IClA^3\Pi_2$	2.6651	4875.520	224.571	0.674	0.0865	1.8823	27.4147	25
10.	$HFX^1\Sigma^+$	0.9168	49384.000	4138.320	772.400	20.9557	89.8800	0.9571	26
11.	$H_2X^1\Sigma_g^+$	0.7416	38297.000	4401.265	3051.300	60.8477	120.6020	0.5039	27
12.	$COX^1\Sigma^+$	1.1283	90529.000	2169.813	17.504	1.93137	13.2883	6.8562	14
13.	$XeOd^1\Sigma^+$	2.8523	693.000	156.832	5.400	0.1456	9.8678	14.2327	28
14.	$Cs_2X^1\Sigma_g^+$	4.6480	3649.500	42.020	0.022	0.0117	0.0826	66.4527	30
15.	$Rb_2X^1\Sigma_g^+$	4.2099	3950.000	57.7807	0.055	0.0224	0.1391	42.4559	31
16.	$XeOb^1\Sigma^+$	2.5480	461.000	113.636	14.593	0.1820	11.8410	14.2651	28
17.	$Ar_2CO_u^+$	3.5960	465.800	66.820	2.500	0.0652	4.0000	19.9810	16
18.	$Ar_2XO_g^+$	3.7610	99.500	30.6800	3.641	0.0596_5	2.4200	19.9810	16
19.	$O_2X^3\Sigma_g^-$	1.2075	42047.000	1579.247	15.466	1.4456	11.5008	7.9975	15
20.	$O_2b_1\Sigma_g^+$	1.2268	28852.000	1432.775	18.198	1.4004	14.0065	7.9975	29
21.	$O_2A^3\Sigma_u^+$	1.5215	6643.000	815.648	18.053	0.9105	19.8513	7.9975	15
22.	$O_2B^3\Sigma_u^-$	1.6042	8121.000	709.050	11.922	0.8189	10.6100	7.9975	15
23.	$O_2^+X^2\Pi_g$	1.1171	54681.000	1905.335	18.970	1.6905	16.3040	7.9973	25
24.	$NOX^2\Pi_{1/2}$	1.1507_7	53323.758	1904.204	17.100	1.6719_5	14.0750	7.4664	14
25.	$NOB^2\Pi$	1.4167	26544.888	1037.200	12.000	1.0920	7.7000	7.4664	14
26.	$N_2X^1\Sigma_g^+$	1.0976	78742.304	2358.570	17.318	1.9982	14.3240	7.0015	14
27.	$N_2A^3\Sigma_u^+$	1.2866	29772.23	1460.640	18.000	1.4546	13.8720	7.0015	14
28.	$N_2a^1\Pi_g$	1.2203	48974.915	1694.208	17.930	1.6169	13.9490	7.0015	14
29.	$N_2B^3\Pi_g$	1.2126	39534.94	1733.390	17.910	1.6374	14.1220	7.0015	14

TABLE II.   Mean square deviations(eqn. 20) from the RKR curves for the various potentials.

S.No.	State	C^a	C_{rel}	ΔY_L (%)	ΔY_V (%)	ΔY_M (%)	ΔY_{FPC} (%)	$\Delta Y_{FPC_{rel}}$ (%)	ΔE_C (%)	$\Delta E_{C_{rel}}$ (%)
1.	$Li_2 X^1\Sigma_g^+$	-0.1460	-0.1298	9.879	8.498	9.952	2.842	2.985	2.576	2.707
2.	$Na_2 X^1\Sigma_g^+$	-0.2024	-0.2031	18.721	16.058	21.372	2.028	2.027	2.878	2.872
3.	$K_2 X^1\Sigma_g^+$	-0.2780	-0.2694	10.448	9.155	13.622	2.034	2.062	1.374	1.409
4.	$Cl_2 X^1\Sigma_g^+$	-0.1097	-0.0910	2.063	2.047	7.628	3.502	3.665	3.105	3.265
5.	$Cl_2 B^3\Pi$	-0.1036	-0.1034	3.971	3.378	7.780	2.258	2.258	2.876	2.874
6.	$I_2 X O_g^+$	-0.1460	-0.1547	1.954	3.416	10.439	2.428	2.474	2.176	2.117
7.	$ICl X^1\Sigma^+$	-0.1000	-0.1020	1.822	1.828	6.842	3.298	3.300	3.306	2.989
8.	$ICl A^3\Pi_1$	-0.1680	-0.1780	3.036	5.452	12.181	1.104	1.244	0.910	0.925
9.	$ICl A^3\Pi_2$	-0.1540	-0.1610	2.171	3.940	10.375	1.260	1.320	0.905	0.882
10.	$HF X^1\Sigma^+$	0.1120	0.1210	4.170	4.313	6.313	3.211	3.245	2.816	2.921
11.	$H_2 X^1\Sigma_g^+$	0.1510	0.1752	5.437	9.986	8.051	3.961	4.153	3.553	3.852
12.	$CO X^1\Sigma^+$	0.0370	0.0460	2.551	3.408	1.210	0.548	0.603	0.292	0.347
13.	$XeO d^1\Sigma^+$	-0.0940	-0.0683	7.478	6.192	7.570	5.183	5.398	5.140	4.957
14.	$Cs_2 X^1\Sigma_g^+$	-0.2949	-0.3114	16.507	14.965	22.449	1.889	2.100	1.601	1.512
15.	$Rb_2 X^1\Sigma_g^+$	-0.2890	-0.2898	10.444	9.271	14.103	2.208	2.207	1.446	1.443
	Average			6.710	6.794	10.659	2.517	2.802	2.348	2.338

^{a}The values are slightly different from those obtained by Wei Hua [9], possibly because of reduced mass which we have taken from ref. 14 for all

the molecules.

TABLE III. Mean square deviations from the RKR curves for the various potentials.

S.No.	State	C_F	ΔY_L (%)	ΔY_V (%)	ΔY_M (%)	$\Delta Y_{FPC_{rel}}$ (%)	$\Delta E_{C_{rel}}$ (%)	E_{max} D_e	Ref.for RKR Potential
1.	$XeOb^1\Sigma^+$	0.5410	20.478	18.962	15.985	5.168	2.984	0.6582	28
2.	$Ar_2CO_u^+$	0.1105	17.744	16.530	14.136	13.406	10.313	0.7022	16
3.	$Ar_2XO_g^+$	-0.0223	7.302	5.967	6.881	6.038	2.015	0.9484	16
4.	$O_2X^3\Sigma_g^-$	-0.0242	1.867	1.998	3.244	2.914	1.745	0.7064	15
5.	$O_2b^1\Sigma_g^+$	-0.0530	0.419	0.484	1.347	0.851	0.381	0.3870	(b)
6.	$O_2A^3\Sigma_u^+$	-0.2372	8.994	11.166	18.781	3.758	2.805	0.9849	15
7.	$O_2B^3\Sigma_u^-$	-0.2500	4.612	5.097	11.171	2.612	0.927	0.9031	15
8.	$O_2^+X^2\Pi_g$	0.0036	0.968	1.220	0.110	0.094	0.102	0.3330	15
9.	$COa^3\Sigma^+$	0.0169	7.654	8.274	5.998	5.951	3.820	0.7664	(b)
10.	$N_2X^1\Sigma_g^+$	-0.0561	2.459	2.095	5.573	4.049	2.787	0.9937	(b)
	Average		7.25	7.18	8.32	4.48	2.79		

[b] RKR potential is calculated using LeRoy's computer program [32].

TABLE IV. Comparison of experimental values of α_e with calculated values and the mean deviations $[\Delta X = (\alpha_e(exptl) - \alpha_e(i))/(\alpha_e(exptl)]$; where $\alpha_e(i)$ stands for, $\alpha_e(FPC_{rel})$, FP; $\alpha_e(M)$, Morse; $\alpha_e(V)$, Varshni; $\alpha_e(L)$, Lippincott for different electronic states.

S.No.	State	C_{rel}	$\alpha_e(exptl)$ $(10^3 cm^{-1})$	$\alpha_e(FPC_{rel})$ $(10^3 cm^{-1})$	$\alpha_e(M)$ $(10^3 cm^{-1})$	$\alpha_e(V)$ $(10^3 cm^{-1})$	$\alpha_e(L)$ $(10^3 cm^{-1})$	$\Delta X_{FPC_{rel}}$ (%)	ΔX_M (%)	ΔX_V (%)	ΔX_L (%)

No.	Species										
1.	$Li_2X^1\Sigma_g^+$	-0.1298	7.040	7.875	10.206	9.137	9.097	11.9	45.0	29.8	29.2
2.	$Na_2X^1\Sigma_g^+$	-0.2031	0.873	0.972	1.449	1.239	1.282	11.4	66.1	42.0	46.9
3.	$K_2X^1\Sigma_g^+$	-0.2694	0.212	0.233	0.394	0.329	0.346	9.9	86.0	55.4	63.5
4.	$Cl_2X^1\Sigma_g$	-0.0910	1.516	1.672	1.903	1.585	1.655	10.3	25.5	4.6	9.1
5.	$Cl_2B^3\Pi$	-0.1034	2.511	2.439	2.793	2.396	2.412	2.8	11.2	4.6	3.9
6.	$I_2XO_g^+$	-0.1547	0.113	0.125	0.154	0.131	0.134	10.1	36.5	15.9	18.1
7.	$IClX^1\Sigma^+$	-0.1020	0.532	0.581	0.670	0.561	0.582	9.2	26.0	5.5	9.3
8.	$IClA^3\Pi_1$	-0.1780	0.744	0.788	1.000	0.867	0.865	5.8	34.8	16.5	16.3
9.	$IClA^3\Pi_2$	-0.1610	0.674	0.717	0.893	0.767	0.772	6.4	32.5	13.7	14.4
10.	$HFX^1\Sigma^+$	0.1210	772.400	801.900	658.200	647.600	593.900	3.8	14.8	16.1	23.1
11.	$H_2X^1\Sigma_g^+$	0.1752	3051.300	3502.874	2229.439	4183.994	2161.944	14.8	26.9	37.1	29.1
12.	$COX^1\Sigma^+$	0.0460	17.504	17.600	16.440	14.080	14.547	0.5	6.0	19.5	16.9
13.	$XeOd^1\Sigma^+$	-0.0683	5.400	5.088	5.520	4.932	4.745	5.8	2.2	8.9	12.1
14.	$Cs_2X^1\Sigma_g^+$	-0.3114	0.022	0.0238	0.0435	0.0361	0.0381	8.8	98.6	64.7	73.9
15.	$Rb_2X^1\Sigma_g^+$	-0.2898	0.055	0.062	0.108	0.0897	0.0947	11.3	95.3	62.4	71.3
16.	$XeOb^1\Sigma^+$	0.5410	14.593	14.900	9.090	7.910	7.842	2.0	37.6	45.7	46.2
17.	$Ar_2CO_u^+$	0.1105	2.500	2.189	1.930	1.670	1.667	12.4	22.6	32.8	33.3
18.	$Ar_2XO_g^+$	-0.0223	3.641	3.580	3.685	3.210	3.176	1.6	1.2	11.8	12.7
19.	$O_2X^3\Sigma_g^-$	-0.0242	15.466	16.870	17.480	14.500	15.311	8.6	13.0	6.2	0.9
20.	$O_2b^1\Sigma_g^+$	-0.0530	18.198	19.500	21.052	17.449	18.364	7.1	15.6	4.1	0.9
21.	$O_2A^3\Sigma_u^+$	-0.2372	18.053	18.290	25.870	22.100	22.360	1.3	43.3	22.4	23.9
22.	$O_2B^3\Sigma_u^-$	-0.2500	11.922	12.810	18.990	15.920	16.478	7.4	59.3	33.6	38.2
23.	$O_2^+X^2\Pi_g$	-0.0036	18.970	19.130	18.880	15.690	16.680	1.7	0.5	17.4	12.2
24.	$NOX^2\Pi_1$	-0.0352	17.100	18.180	19.000	15.770	16.600	5.8	11.1	7.7	2.6
25.	$NOB^2\Pi$	-0.0371	12.000	13.030	13.802	11.500	12.120	8.3	15.0	4.1	1.0
26.	$N_2X^1\Sigma_g^+$	-0.0561	17.318	18.478	20.030	16.710	17.598	6.6	15.6	3.5	1.6
27.	$N_2A^3\Sigma_u^+$	-0.0836	18.000	19.250	21.808	18.070	19.030	6.7	21.1	0.4	5.7
28.	$N_2a^1\Pi_g$	-0.0157	17.930	18.170	18.610	15.500	16.330	1.0	3.7	13.5	8.9
29.	$N_2B^3\Pi_g$	-0.0915	17.910	19.400	22.300	18.490	19.500	8.0	24.6	3.2	8.9

								7.2	27.6	18.7	19.7
	Average							7.2	27.6	18.7	19.7

TABLE V. Comparison of experimental values of $\omega_e x_e$ with calculated values and the mean deviations $[\Delta X = (\omega_e x_e(exptl) - \omega_e x_e(i))/(\omega_e x_e(exptl)]$; where $\omega_e x_e(i)$ stands for $\omega_e x_e(FC_{rel})$, FP; $\omega_e x_e(M)$, Morse; $\omega_e x_e(V)$, Varshni; $\omega_e x_e(L)$, Lippincott; $\omega_e x_e(exp.)$ using equation 29 for the corresponding electronic states given in table 3.

S.No.	$\omega_e x_e(exptl.)$ cm^{-1}	$\omega_e x_e FPC_{rel}$ cm^{-1}	$\omega_e x_e(M)$ cm^{-1}	$\omega_e x_e(V)$ cm^{-1}	$\omega_e x_e(L)$ cm^{-1}	$\omega_e x_e(exp)$ cm^{-1}	$\Delta X_{FPC_{rel}}$ (%)	ΔX_M (%)	ΔX_V (%)	ΔX_L (%)	$\Delta X_e xp$ (%)

1.	2.6100	3.2150	3.6250	3.9500	2.9708	3.1835	23.1	38.8	16.1	13.8	21.9
2.	0.7254	0.8816	1.0518	0.8640	0.8468	0.8585	21.5	45.0	19.1	16.7	18.3
3.	0.3276	0.3859	0.4808	0.3918	0.3814	0.3700	17.8	46.8	19.6	16.4	12.0
4.	2.6943	3.5437	3.8631	3.1681	2.9890	3.5272	31.5	43.4	17.6	10.9	30.9
5.	4.8000	4.4261	4.8800	4.0982	3.7199	4.3991	7.8	1.7	14.6	22.5	8.3
6.	0.6079	0.7973	0.9169	0.7637	0.7016	0.7860	31.2	50.8	25.6	15.4	29.3
7.	1.4920	1.9104	2.1026	1.7328	1.6202	1.8992	28.01	40.9	16.1	8.6	27.3
8.	2.1210	2.4911	2.9185	2.466	2.2206	2.4423	17.4	37.6	16.3	4.7	15.5
9.	1.8823	2.2354	2.5859	2.1712	1.9709	2.2002	18.8	37.4	15.3	4.7	16.9
10.	89.8800	98.4446	86.6965	75.3269	72.8732	97.8364	9.5	3.5	16.2	18.9	8.8
11.	120.6020	152.4790	126.4533	148.9109	117.6726	150.6605	26.4	4.9	23.5	2.4	24.9
12.	13.2883	13.6250	13.0016	13.6854	10.4741	13.6117	2.5	2.2	19.6	21.2	2.4
13.	9.8678	8.3081	8.8731	7.7068	6.7091	8.2869	15.8	10.0	21.9	32.0	16.0
14.	0.0826	0.0950	0.1209	0.09848	0.09510	0.8858	15.1	46.5	19.3	15.2	7.3
15.	0.1391	0.1678	0.2113	0.1721	0.1668	0.1581	20.6	51.9	23.7	19.9	13.6
16.	11.8410	12.8083	7.0028	5.9355	5.3070	11.9983	8.2	40.9	49.8	55.1	1.3
17.	4.0000	2.6900	2.3960	2.0304	1.8202	2.6742	32.8	44.1	49.2	54.5	33.1
18.	2.4200	2.3130	2.3649	2.0126	1.7960	2.3124	4.4	2.3	16.8	25.7	4.4
19.	11.5008	14.4758	14.8287	12.0728	11.6615	14.4715	25.9	28.9	4.9	1.4	25.8
20.	14.0065	16.8908	17.7877	14.5104	13.8627	16.8654	20.6	26.9	3.6	1.0	20.4
21.	19.8513	20.5039	25.0369	20.9516	19.1156	19.7470	3.3	26.1	5.5	3.7	0.5
22.	10.6100	12.5700	15.4769	12.758	11.9120	12.0516	18.4	45.8	20.2	12.3	13.6
23.	16.3040	16.6684	16.5940	13.5247	13.0900	16.6683	2.2	1.8	17.0	19.7	2.2
24.	14.0750	16.1025	16.9990	13.5732	13.1284	16.0920	14.4	20.7	3.6	6.7	14.3
25.	7.7000	9.4823	10.1317	8.0125	7.7847	9.4755	23.1	31.6	4.1	1.1	23.1
26.	14.3240	16.7209	17.6615	14.3895	13.9912	16.6926	16.7	23.3	0.5	2.3	16.5
27.	13.8720	16.5410	17.9149	14.6094	13.9800	16.4767	19.2	29.1	5.3	0.8	18.7
28.	13.9490	14.4239	14.6521	11.9364	11.5933	14.4221	3.4	5.0	14.4	16.9	3.4
29.	14.1220	17.4174	18.9990	15.4808	14.8614	17.3355	23.3	34.5	9.6	5.2	22.7

	Average						17.4	26.9	15.5	13.4	15.9